

**THE CONSTANCY OF STATIC LIQUID JUNCTION
POTENTIALS IN COMPLEX SYSTEMS AND
THEIR APPLICATION TO THE
TITRATION OF WEAK BASES**

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the University of Michigan

By
RICHARD HITCHENS
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POTENTIALS IN CHEMICAL SYSTEMS AND
THEIR APPLICATION TO THE
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Submitted in Partial Fulfillment of the Requirements
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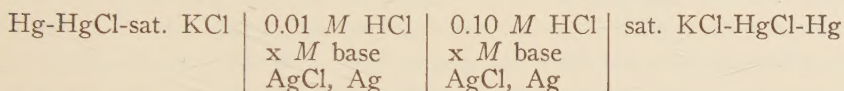
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THE CONSTANCY OF STATIC LIQUID JUNCTION POTENTIALS IN COMPLEX SYSTEMS AND THEIR APPLICATION TO THE TITRATION OF WEAK BASES.¹

By ALFRED L. FERGUSON,² RICHARD HITCHENS³ AND KENNETH VAN LENTE.⁴

ABSTRACT.

Cells of the general type



were studied as to reproducibility and constancy, also as to their possible use for titration of very weak bases. The amount of base was increased in steps up to 0.10 *M*. Three bases were used, ammonium hydroxide, glycine, and aniline. Potentials were plotted against concentration of base for these systems and a more or less definite break was obtained when sufficient base was added to neutralize all of the 0.10 *M* HCl present. The potentials were found to be very reproducible and constant for many hours. This is a possible method for the determination of the combining weight of very weak bases. It was found that the characteristics of these curves were determined appreciably by the reaction of excess base in the more dilute solution with the excess acid in the more concentrated solution, thus forming a salt solution at the boundary.

INTRODUCTION.

In two earlier articles⁵ the authors have described an apparatus for producing static liquid junctions in simple systems, the potentials of which are reproducible and constant. They have concluded from a comparison of the static and the flowing junction boundary that the

¹ The material in this article is constructed from a portion of the thesis submitted to the Graduate School of the University of Michigan by Richard Hitchens, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Manuscript received January 16, 1937.

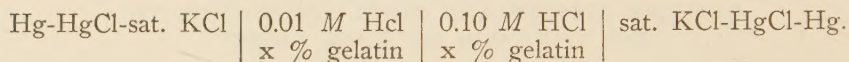
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⁵ Ferguson, Van Lente and Hitchens, *J. Am. Chem. Soc.*, **54**, 1279, 1285 (1932).

former does not depend to so great an extent upon conditions that must be standardized in order to get reproducible results. Also, the work of Ferguson and Bacon⁶ on static liquid junction potentials, in which the combining weight of gelatin was determined, suggested the possibility of obtaining the combining weights of extremely weak bases by boundary potential methods. They made measurements on cells of the type



A series of such cells was used in which the amount of gelatin was varied from low to high values. As indicated, the amount of gelatin, x , added to both sides of the hydrochloric acid concentration cell, was the same. It was found that the junction potential was greater the larger the amount of gelatin for low values of x , and rapidly rose to a peak, then fell suddenly and even changed in sign. A similar set of measurements was made using a system identical with this except that sodium hydroxide was used in place of gelatin. The curves obtained were precisely of the same nature as those just described and the sharp peak came exactly at the equivalence point for the acid and base used. On the basis of the practically identical nature of these two sets of curves it was concluded that the peak represented the point at which equivalent quantities of gelatin and hydrochloric acid were present in the dilute solution, and gave 1,090 grams as the equivalent weight for gelatin, which agrees well with values obtained by other methods. If the substitution of extremely weak bases for the gelatin would still yield a curve with a sharp peak, then this method should constitute a possible means for the titration of such bases. Ordinary means of titration with indicators are useless in these cases. Special physico-chemical methods such as interferometric, conductometric, or potentiometric titrations, and even the so-called corrected methods for the last two, yield poor results.

The purpose of this investigation is then two-fold: to determine if boundary potential measurements on systems formed from a weak base and hydrochloric acid furnish a means of titrating the former, and to see whether such complex systems yield reproducible static liquid junction potentials constant over long periods of time, as was found to be the case for the simple systems described in previous work.⁵

In order to lay a foundation for work with extremely weak bases, it is advisable to use first a moderately weak base, the reaction of which with

⁶ Ferguson and Bacon, *J. Am. Chem. Soc.*, **49**, 1921, 1934 (1927).

acids is well-known from other titrations. Ammonium hydroxide, with a basic dissociation constant of 1.8×10^{-5} serves the purpose well. The method is later applied to the titration of glycine with an apparent basic dissociation constant of 2.1×10^{-12} and to aniline with a basic dissociation constant of 4×10^{-10} .

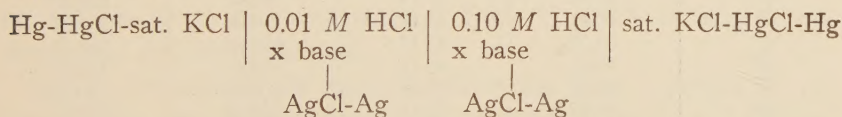
APPARATUS AND MATERIALS.

The calomel electrodes, silver chloride electrodes, thermostat, static junction apparatus, and potential measuring apparatus were similar to those described in an earlier article.⁵ Saturated potassium chloride solution and 0.1 *M* and 0.01 *M* hydrochloric acid also were made in the same way as described earlier. The ammonium chloride used was Mallinckrodt's reagent quality, recrystallized once from water, dried at 110° C., and kept over phosphorus pentoxide. The glycine employed was the Eastman Kodak Company ammonia-free product. Before use, it was dried for several weeks over phosphorus pentoxide. Aniline from aniline sulfate was refluxed for four hours with powdered zinc and then distilled under reduced pressure in an atmosphere of nitrogen. The middle third, a perfectly colorless liquid, was saved. It was kept in the dark in small samples in a desiccator filled with nitrogen.

Ammonium hydroxide solutions were prepared by passing ammonia gas into distilled water. They were diluted until titration with standard hydrochloric acid and methyl red as an indicator showed them to be of the concentrations desired. Instead of mixing ammonium hydroxide and hydrochloric acid, in all cases the proper proportions of hydrochloric acid and ammonium chloride were used, since the desired solutions could be prepared more accurately. All solutions were made in equivalents of solute per 1,000 grams of water, with weighings corrected to vacuum.

EXPERIMENTAL.

The general type of cell used throughout this investigation may be represented by



This cell was constructed and treated in precisely the same manner as described earlier.⁵

In each case the procedure was to start with *x* equal to zero. Potential measurements were then carried out with cells in which *x* pos-

TABLE I.

Potentials Involved in the System

Hg-HgCl-sat. KCl		0.008 M NH ₄ Cl 0.002 M HCl AgCl-Ag	0.008 M NH ₄ Cl 0.092 M HCl AgCl-Ag	sat. KCl-HgCl-Hg	
A		B	C	D	
(1) Time, Hours	(2) Pot. D-A mv.	(3) Pot. D-C mv.	(4) Pot. C-B mv.	(5) Pot. A-B mv.	
0	49.45	45.15	104.58	100.26	
1	49.45	45.13	104.61	100.27	
2	49.45	45.13	104.61	100.28	
3	49.47	45.12	104.62	100.29	
4	49.47	45.12	104.63	100.28	
14	49.49	45.11	104.64	100.25	
15	49.47	45.09	104.64	100.24	
16	49.46	45.08	104.64	100.24	
17	49.46	45.08	104.63	100.24	
18	49.44	45.06	104.61	100.22	
19	49.43	45.05	104.61	100.22	
20	49.41	45.05	104.60	100.23	
21	49.37	45.04	104.55	100.23	
22	49.35	45.06	104.55	100.24	
23	49.33	45.04	104.52	100.25	
24	49.31	45.04	104.52	100.25	
25	49.31	45.03	104.53	100.24	
26	49.31	45.03	104.53	100.24	
Average	49.44	45.10	104.60	100.25	
Av. dev.	± 0.07	± 0.04	± 0.04	± 0.01	
Duplicate Cell.					
0	49.33	45.20	104.42	100.30	
1	49.34	45.21	104.42	100.30	
2	49.35	45.20	104.42	100.29	
3	49.37	45.20	104.45	100.29	
4	49.38	45.20	104.47	100.29	
5	49.39	45.19	104.47	100.29	
6	49.41	45.20	104.49	100.28	
7	49.41	45.20	104.49	100.29	
8	49.42	45.19	104.49	100.28	
9	49.43	45.19	104.49	100.28	
19	49.40	45.14	104.46	100.22	
21	49.41	45.14	104.46	100.21	
23	49.35	45.14	104.44	100.26	
24	49.36	45.15	104.44	100.25	
25	49.32	45.15	104.42	100.26	
26	49.33	45.15	104.42	100.25	
27	49.30	45.17	104.40	100.26	
Average	49.39	45.18	104.45	100.28	
Av. dev.	± 0.03	± 0.02	± 0.03	± 0.02	
Average of two cells	49.42	45.14	104.53	100.27	

essed several definite values from zero to 0.1 *M*. After *x* became greater than 0.01 *M* the use of silver chloride electrodes was discontinued, since obviously they are not applicable to solutions containing free ammonium hydroxide.

The potential differences between the calomel electrodes, between the silver chloride electrodes, and between each calomel electrode and the respective adjacent silver chloride electrode, were measured over periods ranging from 20 to 100 hours in order to obtain data regarding the constancy of each junction potential. To determine the reproducibility of the potentials, a duplicate cell was used in each case. A typical set of data is given in Table I.

The type of cell, including the composition of each solution, is given at the top of the table. The junctions are indicated by vertical lines. The electrodes are lettered A, B, and C, and D to facilitate the tabulation of the potentials. All potentials are given in millivolts. Column one states in each case the time elapsed since the junctions were first formed. The second column, D-A, contains the potentials measured between the saturated calomel electrodes. The third column, D-C, contains the potentials measured between the silver chloride electrodes in the more concentrated solution and the saturated calomel electrode bridged to that solution. Column four, C-B, contains the potentials measured between the silver chloride electrodes in the dilute and in the more concentrated solutions. The fifth column, A-B, gives the same data for the dilute solution that column three does for the concentrated one. Results obtained with a duplicate cell made with the same electrodes but with new solutions and junctions are given in the lower half of the table.

Examination of Table I shows clearly that the potentials of each of the boundaries remain essentially constant over long periods of time.

The degree of constancy and reproducibility of all the potentials may be seen best from an examination of Table II which contains a summary of all the results obtained.

In the first column, the compositions of the dilute solutions, B, are given; in the second, those of the more concentrated solutions C. Column three gives the total number of hours during which the cells were studied. Column four contains the averages of the potentials measured between the two saturated calomel electrodes and the average deviation of the readings. The two values for each pair of solutions are

TABLE II.
Summary of the Average Values for the Cells Involving HCl, NH₄Cl, and NH₄OH.

Dilute Soln.	Conc. Soln.	Time Meas.	Pot. mv. D-A	Pot. mv. D-C	Pot. mv. C-B	Pot. mv. A-B
0.01 M HCl	0.10 M HCl	48	38.12 $\pm$ 0.05	45.33 $\pm$ 0.03	92.46 $\pm$ 0.01	99.64 $\pm$ 0.05
0.004 M NH ₄ Cl	0.004 M NH ₄ Cl	34	42.65 $\pm$ 0.04	45.05 $\pm$ 0.05	97.38 $\pm$ 0.04	98.77 $\pm$ 0.11
0.006 M HCl	0.096 M HCl	27	42.56 $\pm$ 0.05	44.94 $\pm$ 0.05	97.28 $\pm$ 0.03	99.69 $\pm$ 0.05
0.008 M NH ₄ Cl	0.008 M NH ₄ Cl	26	49.44 $\pm$ 0.07	45.10 $\pm$ 0.04	104.60 $\pm$ 0.04	100.25 $\pm$ 0.01
0.002 M HCl	0.092 M HCl	27	49.39 $\pm$ 0.03	45.18 $\pm$ 0.02	104.45 $\pm$ 0.03	100.28 $\pm$ 0.02
0.009 M NH ₄ Cl	0.009 M NH ₄ Cl	36	51.66 $\pm$ 0.07	45.07 $\pm$ 0.02	107.08 $\pm$ 0.12	100.50 $\pm$ 0.06
0.001 M HCl	0.091 M HCl	33	51.83 $\pm$ 0.10	45.06 $\pm$ 0.03	107.20 $\pm$ 0.07	100.42 $\pm$ 0.01
0.01 M NH ₄ Cl	0.01 M NH ₄ Cl	34	54.25 $\pm$ 0.03	45.25 $\pm$ 0.02	109.64 $\pm$ 0.03	100.68 $\pm$ 0.01
0.000 M HCl	0.09 M HCl	52	54.31 $\pm$ 0.07	45.23 $\pm$ 0.03	109.75 $\pm$ 0.04	100.67 $\pm$ 0.01
0.01 M NH ₄ Cl	0.015 M NH ₄ Cl	27	47.50 $\pm$ 0.01			
0.005 M NH ₄ OH	0.085 M HCl					
0.01 M NH ₄ Cl	0.02 M NH ₄ Cl	65	42.36 $\pm$ 0.05			
0.01 M NH ₄ OH	0.08 M HCl					
0.01 M NH ₄ Cl	0.05 M NH ₄ Cl	28	21.78 $\pm$ 0.06			
0.04 M NH ₄ Cl	0.05 M NH ₄ OH					
0.01 M NH ₄ Cl	0.10 M NH ₄ Cl	43	0.48 $\pm$ 0.02			
0.09 M NH ₄ OH						

for the duplicate cells. Columns five, six, and seven contain similar data for the other three sets of potentials measured. The potentials under the various headings correspond to those under the same heading in Table I.

An inspection of Table II shows that all of the potentials are remarkably constant. The variations in the two side junctions between saturated potassium chloride solutions and the two other solutions become

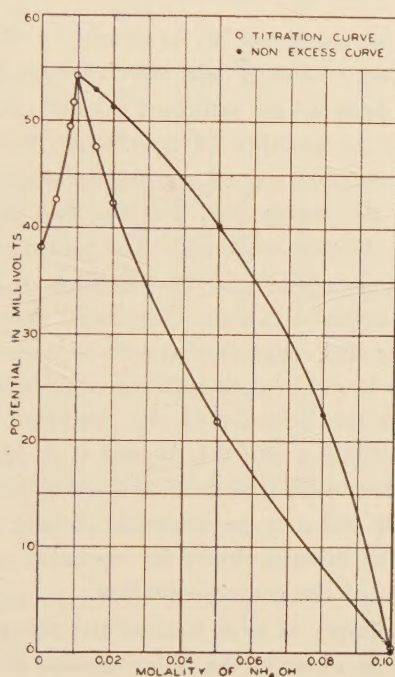


FIG. 1.

especially small as the proportion of ammonium chloride increases, *i. e.*, for successive cells from the top to the bottom of the columns in the summary. In general, the potential changes in the central boundary are larger than those in the others, while those of the whole cell are about the same as those of the center boundary. The mean of the average deviations of the forty-two sets of measurements in Table II is only 0.04 mv.

The reproducibility of the potentials is slightly less than their constancy, as might be expected. The differences in the averages of duplicate cells vary from 0.01 mv. to 0.17 mv., although the majority are less

than 0.1 mv. The fact that the mean of the differences between the averages of sixteen pairs of duplicate measurements is only 0.07 mv. indicates clearly that the potentials are highly reproducible.

The results given in Tables I and II prove conclusively that static liquid junctions made as described earlier⁵ possess reproducible potentials constant over long periods of time with the complex systems studied in this investigation, as well as with the simple systems used in the former work.

The change of junction potentials produced by the addition of ammonium hydroxide may be seen best from the graph in Fig. 1. The potentials measured between the saturated calomel electrodes are plotted as ordinates against the molality of ammonium hydroxide present as abscissae. These potentials are, of course, the algebraic sum of three junction potentials, the center one, and the two side ones involving saturated potassium chloride solutions. The measured potential will be that of the center boundary only if the potentials of the two side junctions are equal and opposite in sign. Scatchard⁷ has claimed this to be true for hydrochloric acid concentration cells of concentrations less than 0.1 *M*. The authors found in their earlier work,⁵ however, that there is enough difference in the behavior of the junctions between saturated potassium chloride solution and 0.1 *M* and 0.01 *M* hydrochloric acid respectively to warrant belief that these two junctions are somewhat different in nature. It still may be assumed, though, that the potentials measured between the calomel electrodes represent to a high degree of approximation those of the center boundary.

The curve rises sharply at first because the relative decrease of the activity of the hydrogen ions in the dilute solution is much greater than that in the concentrated solution. At the peak of the curve the dilute solution is 0.01 *M* ammonium chloride and the concentrated one is 0.01 *M* with respect to ammonium chloride and 0.09 *M* with respect to hydrochloric acid. At this point the curve suddenly breaks downward sharply, being concave upward all the way down to its final value of 0.48 mv. The sharpness of the break in this curve at the 0.01 *M* point shows conclusively that such junction potential measurements may be used in the quantitative titration of ammonium hydroxide with hydrochloric acid. The quantitative nature of these results suggests the possible application of the method to extremely weak bases.

⁷ Scatchard, J. Am. Chem. Soc., **47**, 696 (1925).

TABLE III.
Summary of Potential Measurements of Cells Containing *HCl* and *Glycine*.

Dilute Soln.	Conc. Soln.	Time Meas.	Pot. mv. D-A	Pot. mv. D-C	Pot. mv. C-B	Pot. mv. A-B
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>	48	38.12 $\pm$ 0.05	45.33 $\pm$ 0.03	92.46 $\pm$ 0.01	99.64 $\pm$ 0.05
0.004 <i>N</i> <i>Glycine</i>	0.004 <i>N</i> <i>Glycine</i>	27	40.43 $\pm$ 0.06	45.47 $\pm$ 0.02	94.95 $\pm$ 0.02	100.00 $\pm$ 0.02
0.01 <i>N</i> <i>HCl</i>	0.100 <i>N</i> <i>HCl</i>	20	40.45 $\pm$ 0.02	45.51 $\pm$ 0.04	94.94 $\pm$ 0.02	99.99 $\pm$ 0.01
0.008 <i>N</i> <i>Glycine</i>	0.008 <i>N</i> <i>Glycine</i>	24	42.07 $\pm$ 0.01	45.14 $\pm$ 0.02	95.22 $\pm$ 0.01	98.27 $\pm$ 0.01
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>	21	42.06 $\pm$ 0.01	45.14 $\pm$ 0.01	95.24 $\pm$ 0.02	98.31 $\pm$ 0.01
0.009 <i>N</i> <i>Glycine</i>	0.009 <i>N</i> <i>Glycine</i>	26	42.39 $\pm$ 0.02	45.37 $\pm$ 0.02	95.80 $\pm$ 0.06	98.77 $\pm$ 0.02
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>	21	42.37 $\pm$ 0.02	45.35 $\pm$ 0.02	95.78 $\pm$ 0.01	98.76 $\pm$ 0.02
0.01 <i>N</i> <i>Glycine</i>	0.01 <i>N</i> <i>Glycine</i>	24	42.67 $\pm$ 0.05	45.04 $\pm$ 0.01	95.53 $\pm$ 0.03	97.92 $\pm$ 0.03
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>	21	42.75 $\pm$ 0.04	45.15 $\pm$ 0.02	95.78 $\pm$ 0.01	98.19 $\pm$ 0.04
0.0125 <i>N</i> <i>Glycine</i>	0.0125 <i>N</i> <i>Glycine</i>	39	42.74 $\pm$ 0.01	45.02 $\pm$ 0.02	95.39 $\pm$ 0.01	97.67 $\pm$ 0.04
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>					
0.015 <i>N</i> <i>Glycine</i>	0.015 <i>N</i> <i>Glycine</i>	25	42.69 $\pm$ 0.05	45.09 $\pm$ 0.03	94.87 $\pm$ 0.04	97.26 $\pm$ 0.05
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>					
0.02 <i>N</i> <i>Glycine</i>	0.02 <i>N</i> <i>Glycine</i>	22	41.66 $\pm$ 0.05	45.44 $\pm$ 0.02	92.77 $\pm$ 0.05	96.57 $\pm$ 0.04
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>					
0.04 <i>N</i> <i>Glycine</i>	0.04 <i>N</i> <i>Glycine</i>	27	31.96 $\pm$ 0.10	45.45 $\pm$ 0.04	83.59 $\pm$ 0.08	97.01 $\pm$ 0.15
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>					
0.06 <i>N</i> <i>Glycine</i>	0.06 <i>N</i> <i>Glycine</i>	30	21.04 $\pm$ 0.04	45.19 $\pm$ 0.03	71.68 $\pm$ 0.24	95.83 $\pm$ 0.26
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>					
0.01 <i>N</i> <i>Glycine</i>	0.10 <i>N</i> <i>Glycine</i>	65	3.38 $\pm$ 0.03	44.89 $\pm$ 0.08	53.87 $\pm$ 0.35	95.29 $\pm$ 0.37
0.01 <i>N</i> <i>HCl</i>	0.10 <i>N</i> <i>HCl</i>					

The next material studied was glycine. This material was used both because of its weakly basic properties and because it is a hydrolysis product of gelatin. Gelatin itself gave such beautiful results when it was titrated by this method⁶ that one might expect its hydrolysis products to give as good or better. The type of cell used and the procedure were identical with those described above.

A summary of the results obtained with the glycine-hydrochloric acid systems is given in Table III.

Examination of the data shows that with these systems, also, the static junction is capable of an extremely high degree of constancy. For some reason the constancy of potential of silver chloride electrodes in the dilute solutions containing a large excess of free glycine is poor. The large deviations in potential for the last three cells in the columns headed C-B, and A-B are caused entirely by changes in potential of the silver chloride electrodes in solution B, since the two potentials C-B and A-B always changed the same amount in the same direction and the potentials measured with all the other electrodes showed no such variations. Many sets of silver chloride electrodes showed the same lack of constancy. Excluding these last three sets of measurements, 46 sets of results show a mean average deviation of only 0.03 mv.

The reproducibility of the potentials is again less than their constancy. The fact that the mean of the differences between the averages of 36 sets of duplicate measurements is only 0.06 mv. indicates clearly that the potentials are highly reproducible.

The third material used was aniline. The potential measurements with the aniline-hydrochloric acid systems are given in Table IV. The manner of presenting the data is identical with that used in Table I.

The mean of the average deviation of 36 sets of measurements in Table IV is 0.06 mv. which is slightly larger than that for the previous systems.

Duplicate cells were not studied since the reproducibility of the static junction had been demonstrated with the previous systems and since, also, the main purpose of the measurements with aniline was to determine the nature of the titration curve.

The change of junction potential produced by the addition of glycine may be seen from Fig. 2. As ordinates are plotted the potentials measured between the saturated calomel electrodes, as abscissae, the molality of the solutions with respect to glycine.

TABLE IV.
Summary of Potential Measurements of Cells Containing HCl and Aniline.

Dilute Soln.	Conc. Soln.	Time Meas.	Pot. mv. D-A	Pot. mv. D-C	Pot. mv. C-B	Pot. mv. A-B
0.01 N HCl	0.10 N HCl	48	38.12 $\pm$ 0.05	45.33 $\pm$ 0.03	92.46 $\pm$ 0.01	99.64 $\pm$ 0.05
0.004 N Aniline 0.01 N HCl	0.004 N Aniline 0.10 N HCl	25	43.33 $\pm$ 0.07	45.94 $\pm$ 0.05	98.16 $\pm$ 0.03	100.76 $\pm$ 0.03
0.008 N Aniline 0.01 N HCl	0.008 N Aniline 0.10 N HCl	29	51.39 $\pm$ 0.07	45.83 $\pm$ 0.05	106.38 $\pm$ 0.06	100.75 $\pm$ 0.09
0.009 N Aniline 0.01 N HCl	0.009 N Aniline 0.10 N HCl	20	54.03 $\pm$ 0.03	46.47 $\pm$ 0.02	109.15 $\pm$ 0.04	101.59 $\pm$ 0.02
0.01 N Aniline 0.01 N HCl	0.01 N Aniline 0.10 N HCl	24	55.83 $\pm$ 0.06	45.83 $\pm$ 0.05	111.63 $\pm$ 0.07	101.62 $\pm$ 0.02
0.011 N Aniline 0.01 N HCl	0.011 N Aniline 0.10 N HCl	28	55.79 $\pm$ 0.10	45.76 $\pm$ 0.04	112.60 $\pm$ 0.18	102.58 $\pm$ 0.08
0.0125 N Aniline 0.01 N HCl	0.0125 N Aniline 0.10 N HCl	29	53.08 $\pm$ 0.20	45.95 $\pm$ 0.14	108.36 $\pm$ 0.13	101.30 $\pm$ 0.09
0.02 N Aniline 0.01 N HCl	0.02 N Aniline 0.10 N HCl	24	41.72 $\pm$ 0.05	47.04 $\pm$ 0.02	96.74 $\pm$ 0.05	102.07 $\pm$ 0.04
0.06 N Aniline 0.01 N HCl	0.06 N Aniline 0.10 N HCl	28	7.39 $\pm$ 0.15	48.92 $\pm$ 0.02	59.65 $\pm$ 0.05	101.19 $\pm$ 0.10
0.10 N Aniline 0.01 N HCl	0.10 N Aniline 0.10 N HCl	24	— 17.91 $\pm$ 0.00	48.63 $\pm$ 0.01	35.31 $\pm$ 0.01	101.84 $\pm$ 0.01

It is apparent that the curve is considerably different from that obtained with ammonium hydroxide. It rises but slightly to a peak value only 5 mv. above the starting potential. Instead of breaking downward sharply at the 0.01 M point, as did the ammonium hydroxide curve, it remains practically horizontal until the 0.015 M point is reached and then drops off slowly to a final value of 3.38 mv.

The rapid rise in potential in the case of ammonium hydroxide was explained by the relatively rapid decrease of the hydrogen ion activ-

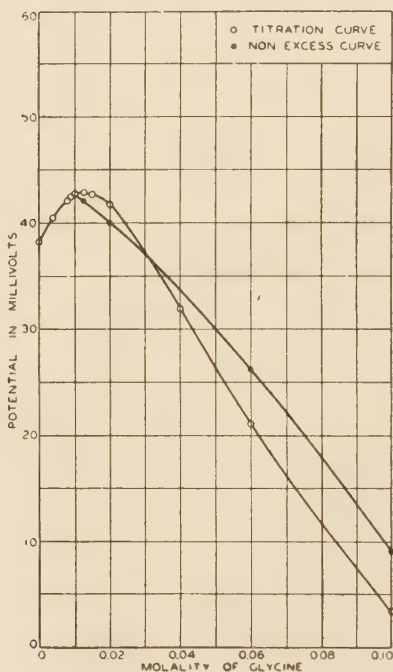


FIG. 2.

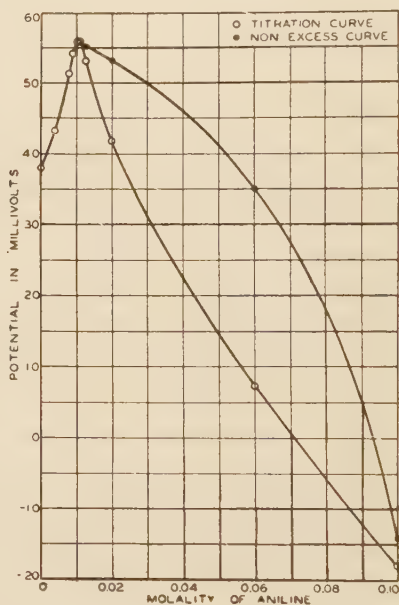


FIG. 3.

ity in the dilute solution. The small rise obtained with glycine indicates that there is appreciable hydrolysis of the glycine hydrochloride. On this account the boundary potential method for titrating weak bases is not quantitatively applicable to such extremely weak bases as glycine. The break obtained with this method is, however, more pronounced and less empirical than that obtained with the "corrected" potentiometric titration.

A similar set of measurements was run with glutamic acid-hydrochloric acid systems. The reproducibility and constancy of the poten-

tials and the shapes of the curves obtained were entirely similar to those just described for glycine and, therefore, are not included in this report.

The fact that Ferguson and Bacon⁶ obtained a much higher and sharper peak with gelatin than was obtained here with glycine and with glutamic acid indicates gelatin to be more strongly basic than these two of its hydrolysis products.

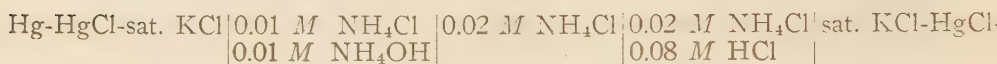
The curve obtained with aniline, a base intermediate in strength between ammonium hydroxide and glycine, is given in Fig. 3. It rises to a peak even higher than that obtained with ammonium hydroxide but, instead of falling precipitously like the latter, shows a slight rounding effect. This rounded peak indicates that while the equivalent weight of a base as weak as aniline may be determined fairly accurately, still it cannot be found quantitatively by this method.

So far in this work the same amount of base x was added to both the 0.01 M HCl and 0.1 M HCl even after an amount of base equivalent to the 0.01 M HCl had been added. Evidently, from this point on, the dilute side contained an excess of the weak base. Since these bases were all very weak, it was the belief they would furnish no ions to the solution and, therefore, have very little if any effect on the liquid junction potential. To test this point, however, new titrations were carried out in which the base was not added to the dilute acid after the acid in that chamber had been neutralized. The values were the same, of course, as those presented above, up to the point of neutralization of the 0.01 M acid. The results of these new titrations are represented in Fig. 1, 2 and 3 by the curves passing through the solid circles.

The differences between the curves after the 0.01 M acid has been neutralized is pronounced in all cases. These differences, however, cannot be ascribed to the ions produced by the excess base since it is so slightly ionized. A possible explanation is that the excess base in the one solution reacts with the excess acid in the other to form at their surface of contact a layer of salt solution which separates the two solutions from one another. Such an interposed layer would act as a salt bridge, tending to reduce the junction potential, especially if the ions of the salt had about the same mobility; the reduction would be greater the higher the concentration of salt formed.

The concentration of such a layer of salt solution would be approximately equivalent to the total amount of base added to the dilute side. If this explanation be correct, then such a concentration of salt placed

between the two solutions should nearly reproduce the potential obtained when the two solutions were directly in contact. A cell to test this explanation was constructed as follows:



The average potential of this cell was 41.15 mv., while that of the corresponding cell in which the solutions were joined directly was 42.36 mv. The agreement is close enough to confirm the explanation for the differences between the curves in Fig. 1. It appears, therefore, that the titration curves described in this paper owe their breaks, to some extent, to the partial elimination of the boundary potential by the interposed salt solution which results from the reaction of excess acid and base at the junction.

As a further test of this conclusion, another cell was used to show that a greater concentration of ammonium chloride, substituted as the intermediate solution, would lower the liquid junction potential even more. A cell with a 0.04 *M* salt solution interposed at the boundary gave a junction potential of 32.99 mv., which is 8.16 mv. less than that produced by the 0.02 *M* salt solution. Only the interplacing of a salt solution, the molality of which was the same as that actually formed when the two solutions were directly in contact, would yield exactly the same potential.

Ferguson and Bacon observed a corresponding difference between the potentials obtained with and without excess gelatin in their dilute solutions and an explanation similar to that offered here was suggested at that time.

From Fig. 2 it is evident that the action in the case of glycine is appreciably different. This is probably due to the excessive hydrolysis of the glycine hydrochloride formed which prevents it from forcing the junction potential to such low values as did the same molality of ammonium chloride. In fact, at the peak of the glycine curve there are three factors influencing the junction potential: (1) the diminished activity of the hydrogen ion in the dilute solution tends to increase the potential; (2) the diminished activity of the hydrogen ion in the concentrated solution tends to decrease the potential; (3) the reaction between free hydrochloric acid and free glycine tends to decrease the potential.

Evidently factor 1 has a more pronounced effect at the true end point where the hydrogen ion activity is still appreciable due to

hydrolysis. Thus, in this region the titration curve should rise above that obtained with solutions containing no excess glycine. As the concentration of glycine is increased, the influence of factor 1 becomes less and that of 2 and 3 becomes more pronounced. Consequently the titration curve must begin to descend and finally fall below that obtained with no excess of glycine. It is impossible, therefore, to get a sharp break at the peak of such a titration curve unless factor 1 is small, *i. e.*, unless the salt formed is but slightly hydrolyzed.

In the case of aniline, Fig. 3, the titration curve also rises slightly above the other for a short distance at the peak. The effect of the reaction at the junction soon becomes apparent, however, and the curve falls rapidly. Even with the four per cent hydrolysis of the 0.01 *M* aniline hydrochloride, the rounding effect is only slight.

SUMMARY.

1. Static liquid junctions, reproducible and constant in potential, have been formed with ammonium hydroxide-hydrochloric acid, glycine-hydrochloric acid and with aniline-hydrochloric acid systems. The first system yielded results which showed an average deviation of only ± 0.04 mv. for thirty hours. The mean of the differences between the averages of sixteen pairs of duplicate cells is only 0.07 mv. The constancy and reproducibility for the other systems is approximately the same as for the first.

2. The liquid junction potential method of titration was found to be quantitative for the titration of ammonium hydroxide with hydrochloric acid, fairly quantitative for the aniline hydrochloric acid, but only approximate for the glycine hydrochloric acid titrations. The break in the latter, however, is more pronounced and depends less upon variable conditions than that obtained in the co-called "corrected" potentiometric titration.

3. An explanation has been given for the shapes of the liquid junction potential titration curves.

4. The effectiveness of the liquid junction potential method for titrating weak bases has been shown to be due to some extent to reaction between free base and free acid at the junction.

